E201 995

GE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 18, 1994	Reprint

4. TITLE AND SUBTITLE

Ion chemistry of $ClONO_2$ involving NO_3^- core ions: A detection scheme for $ClONO_2$ in the atmosphere

5. FUNDING NUMBERS

61102F
P 2303
T GJ
WU01

6. AUTHOR(S)

A.A. Viggiano, Robert A. Morris, Jane M. Van Doren*

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Phillips Lab/GPID
29 Randolph Road
H anscom AFB, MA 01731-3010

8. PERFORMING ORGANIZATION REPORT NUMBER

PL-TR-94-2137

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*Dept of Chemistry, College of the Holy Cross, Worcester, MA

Reprinted from Journal of Geophysical Research, Vol. 99, No. D4, pages 8221-8224, April 20, 1994

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; Distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Abstract. Rate constants and product branching ratios for reactions involving atmospherically interesting ions and $ClONO_2$ have been measured. H_3O^+ reacts rapidly with $ClONO_2$, but hydrates of H_3O^+ do not. This implies that $ClONO_2$ does not play a central role in the positive ion chemistry of the atmosphere. CO_3^- reacts with $ClONO_2$ to form NO_3^-. Both NO_3^- and $NO_3^-(H_2O)$ react with $ClONO_2$ to form $NO_3^-(ClONO_2)$. H_2O does not react with $NO_3^-(ClONO_2)$, which is essential to the proposed in situ measurement technique. $NO_3^-(ClONO_2)$ does react with HNO_3 and HCl, producing $NO_3^-(HNO_3)$ in both cases. The reaction of $NO_3^-(HCl)$ with $ClONO_2$ also produces $NO_3^-(HNO_3)$. These latter two efficient reactions, which are discussed in detail in a separate publication, are analogous to the efficient neutral heterogeneous reaction of HCl with $ClONO_2$ which is important in the chemistry of the Antarctic stratosphere. A detection scheme is presented for atmospheric $ClONO_2$ based on the reactions studied and utilizing mass spectrometry. A $ClONO_2$ detection limit of 10^7 molecules cm^{-3} is estimated based on the operating characteristics of current ion-molecule based mass spectrometric field instruments.

14. SUBJECT TERMS

Chlorine nitrate, Atmosphere, Ion chemistry, Atmosphere

15. NUMBER OF PAGES

4

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. D4, PAGES 8221–8224, APRIL 20, 1994

Ion chemistry of $ClONO_2$ involving NO_3^- core ions: A detection scheme for $ClONO_2$ in the atmosphere

A. A. Viggiano and Robert A. Morris

Geophysics Directorate, Ionospheric Effects Division, Hanscom Air Force Base, Massachusetts

Jane M. Van Doren

Department of Chemistry, College of the Holy Cross, Worcester, Massachusetts

Abstract. Rate constants and product branching ratios for reactions involving atmospherically interesting ions and $ClONO_2$ have been measured. H_3O^+ reacts rapidly with $ClONO_2$, but hydrates of H_3O^+ do not. This implies that $ClONO_2$ does not play a central role in the positive ion chemistry of the atmosphere. CO_3^- reacts with $ClONO_2$ to form NO_3^-. Both NO_3^- and $NO_3^-(H_2O)$ react with $ClONO_2$ to form $NO_3^-(ClONO_2)$. H_2O does not react with $NO_3^-(ClONO_2)$, which is essential to the proposed in situ measurement technique. $NO_3^-(ClONO_2)$ does react with HNO_3 and HCl, producing $NO_3^-(HNO_3)$ in both cases. The reaction of $NO_3^-(HCl)$ with $ClONO_2$ also produces $NO_3^-(HNO_3)$. These latter two efficient reactions, which are discussed in detail in a separate publication, are analogous to the efficient neutral heterogeneous reaction of HCl with $ClONO_2$ which is important in the chemistry of the Antarctic stratosphere. A detection scheme is presented for atmospheric $ClONO_2$ based on the reactions studied and utilizing mass spectrometry. A $ClONO_2$ detection limit of 10^7 molecules cm^{-3} is estimated based on the operating characteristics of current ion-molecule based mass spectrometric field instruments.

Introduction

The details of the chemical cycling of inorganic chlorine species and nitrogen oxide species (NO_y) in the stratosphere are critical to our understanding of stratospheric ozone chemistry. In the presence of polar stratospheric clouds (PSCs), the heterogeneous reactions of the chlorine reservoir species $ClONO_2$, HCl, and HOCl chemically transform these long-lived species into photoactive species which can lead to rapid and catalytic destruction of ozone. In the midlatitude stratosphere and in the absence of PSCs, the combination of photochemical life cycles of these species results in a relatively stable ozone concentration. The chemical life cycle of chlorine nitrate is especially important to the chemistry of the stratosphere because it is a member of both the inorganic chlorine and NO_y families. As such, chlorine nitrate couples these two important chemical families. Understanding the complex chemistry and changing concentration of chlorine nitrate is critical to a complete understanding of the chemistry of the atmosphere.

Despite the importance of chlorine nitrate to the chemistry of the stratosphere, few in situ measurements of its concentration in the atmosphere have been made [*Rinsland et al.*, 1985; *Raper et al.*, 1987; *Toon et al.*, 1993]. Current measurements include column abundance determinations, where a vertical profile is estimated from the spectral line shape [*Toon et al.*, 1993]. Detailed models of stratospheric chemistry, however, do not generally use these values of $ClONO_2$ but rather deduce the concentration of $ClONO_2$ from measurements of related species [*Salawitch et al.*, 1993]. Many models assume that total inorganic chlorine is essentially divided between HCl and $ClONO_2$ (in the absence of PSCs) and therefore calculate the concentration of $ClONO_2$ from the difference between the total inorganic chlorine concentration, derived from N_2O measurements, and the measured HCl concentration [*Salawitch et al.*, 1993; *Webster et al.*, 1993]. Recently, *Webster et al.* [1993] made the first in situ spectroscopic determinations of the HCl concentration in the stratosphere. Their values, measured outside of the polar vortices, differ from previous determinations by as much as a factor of 2 [*Raper et al.*, 1987; *Webster et al.*, 1993]. If total inorganic chlorine is partitioned between HCl and $ClONO_2$, their measurements indicate that there is a corresponding error in the accepted $ClONO_2$ values [*Rodriguez*, 1993; *Webster et al.*, 1993]. The discrepancies between these different determinations represent significant differences in our overall understanding of the chemistry of the stratosphere. A direct in situ measurement of the concentration of $ClONO_2$ in the stratosphere would contribute significantly to a resolution of these discrepancies.

In situ ion composition measurements have proven to be a valuable tool in determining atmospheric concentrations of trace neutral species when combined with the knowledge of the chemistry and rate constants involved. Determination of concentrations of naturally abundant atmospheric species using ion chemistry has been developed mainly by the research groups of Arnold and Eisele, and their work has recently been reviewed by *Viggiano* [1993]. Detection of neutral species can be achieved by measurements of ambient atmospheric ions or, in a more elaborate apparatus, by measurements of product ions formed from reaction with ions produced in an active ion source. These mass spectrometric techniques combine the selectivity of ion-molecule

Paper number 94JD00425.
0148-0227/94/94JD-00425$05.00

chemistry with the sensitivity of mass spectrometry to yield a very powerful detection technique for neutral species abundant in only trace amounts. Measurements of a number of species in the parts per quadrillion range have been made. Negative ion composition measurements have been very successful in determining the concentrations of NO_x and HNO_x species [*Arnold et al.*, 1992; *Viggiano*, 1993]. However, no detection scheme has been successfully devised previously for $ClONO_2$. In this paper we report kinetics measurements involving NO_3^- core ions and $ClONO_2$, the latter species as both a ligand and a neutral reactant. We believe these data will make in situ determinations of the atmospheric $ClONO_2$ concentration possible using currently available mass spectrometric ion detection field instruments.

Experiment

The measurements were made using the Phillips Laboratory variable temperature-selected ion flow drift tube apparatus [*Viggiano et al.*, 1990]. Instruments of this type have been the subject of review [*Smith and Adams*, 1988], and only those aspects important to the present study will be discussed in detail. Ions were created by electron impact in a high-pressure ion source (~0.1–1 torr). The ions were extracted from the source, mass selected in a quadrupole mass filter, and injected into a flow tube. Buffer gas was added through a Venturi inlet surrounding the ion injection orifice and transported the ions along the length of the flow tube. The Venturi inlet aids in injecting the ions at low energy, critical to the present experiments. Downstream, after the ions have had sufficient collisions with the buffer to thermalize, the neutral reactant is added. At the end of the flow tube, a small fraction of the ions are sampled through a 0.2-mm hole in a nose cone. The ions sampled are mass analyzed in a second quadrupole mass spectrometer and detected by a channel electron multiplier. Flow rates of the buffer and of the reactant gas were controlled and measured by MKS flow controllers. The entire flow tube could be heated or cooled. As will be explained below, cooling was necessary to perform some of the experiments presented. Rate constants were determined from the decay of the primary ion signal as a function of added neutral flow.

The weakly bonded cluster ions used in the present experiments required mild conditions to minimize both collisional breakup upon injection and thermal dissociation in the flow tube. NO_3^- and $NO_3^-(HNO_3)$ were made from NO_2 and a several percent HNO_3 impurity in our NO_2 sample. $NO_3^-(HNO_3)$ is a strongly bonded cluster ion, and no special conditions were needed for working with it except low-injection energy. In contrast, it was quite difficult to form, inject, and detect a sufficient concentration of $NO_3^-(H_2O)$. This ion was made from a mixture of NO_2 and H_2O. Our problems were traced to three sources: (1) instability of the ion in the ion source, (2) breakup of the ion upon injection and (3) thermal dissociation in the flow tube. First attempts at injecting $NO_3^-(H_2O)$ into a He buffer at room temperature proved unsuccessful. We observed mainly NO_3^- ion signal and a small mass 80 signal which we later identified as SO_3^- (formed from impurities in the source from previous experiments) and not $NO_3^-(H_2O)$. In order to make a sufficient quantity of $NO_3^-(H_2O)$ we needed both to cool the system and to use a H_2 buffer. The cooling was necessary to prevent thermal dissociation in the buffer gas, which is a problem at room temperature. This is based on the knowledge of the known association rate constant [*Ikezoe et al.*, 1987] and thermodynamics [*Keesee and Castleman*, Jr., 1986] through $K = k_f/k_r$. The use of a H_2 buffer lowers the center of mass energy upon injection for the same laboratory frame energy [*Viggiano*, 1984]. Even with these steps, about equal parts of NO_3^- and $NO_3^-(H_2O)$ were initially present in the flow tube. The presence of both these ions does not affect our rate constant measurements. Both of these ions produce only $NO_3^-(ClONO_2)$, and therefore product determination also was unaffected. $NO_3^-(ClONO_2)$ was made by adding NO_2 and $ClONO_2$ to the source. Creation, injection, and detection of $NO_3^-(ClONO_2)$ was easier than $NO_3^-(H_2O)$ but more difficult than $NO_3^-(HNO_3)$, reflecting the intermediate cluster bond strength of $NO_3^-(ClONO_2)$. $H_3O^+(H_2O)_n$ ions were made from H_2O, and CO_3^- was formed from CO_2.

The $ClONO_2$ was synthesized from ClF and HNO_3 by the method of *Shack* [1967] with some modification [*Lloyd*, 1993] and stored at 200 K. During the experiments, the $ClONO_2$ was heated to 233 K, and the vapor was added to the flow tube through a mass flow controller. At this temperature, little of the HNO_3 impurity present in the sample should be volatile. The flow rate of $ClONO_2$ was calibrated by using the heat capacity given by *Miller et al.* [1967]. In initial experiments the $ClONO_2$ sample was found to contain a large amount of HNO_3. After flowing the $ClONO_2$ for a time period of the order of an hour or two, the HNO_3 impurity was greatly reduced, presumably through conditioning of the inlet lines; that is, water on the inlet line surfaces had reacted away. The experiments required the use of a large amount of $ClONO_2$ which limited the number of reactions studied to date because of limited sample quantity, and further studies are planned. We estimate the uncertainty in our rate constants to be ±30% and the relative error to be 20%, slightly higher than our usual error limits.

Results

Table 1 lists the reactions studied and the temperatures at which the rate constants were measured. As explained in the experimental section, different ions were best studied at different temperatures. The limited amount of $ClONO_2$ sample we could obtain prevented us from making extensive temperature dependence measurements. Temperature dependence studies are planned for the future.

The group of reactions listed in Table 1 was chosen for the potential importance in the atmosphere both in terms of the chemistry of ambient ions and for detection of $ClONO_2$. The series $H_3O^+(H_2O)_n$ can be considered the starting point for much of the positive ion chemistry of the lower atmosphere, with the $n = 3$ or higher species being by far the predominant ions [*Ferguson and Arnold*, 1981]. The present results show that $ClONO_2$ does not react with $H_3O^+(H_2O)_{\geq 2}$. Essentially, all other positive ions in the lower atmosphere are more stable than $H_3O^+(H_2O)_n$ and will presumably also be unreactive toward $ClONO_2$. Therefore the positive ion chemistry of the atmosphere is essentially unaffected by the presence of $ClONO_2$.

The most important ambient negative ions are the series $NO_3^-(HNO_3)_n$ with $n = 1$ to 3 being the most abundant [*Viggiano and Arnold*, 1983]. Above 30 km, the series $HSO_4^-(H_2SO_4)_m(HNO_3)_n$ also becomes important. The present results show that $NO_3^-(HNO_3)$ does not react ap-

Table 1. Rate Constants for Reactions Involving $ClONO_2$

Reaction	Rate Constant, $cm^3\ s^{-1}$	Temperature, K
(1) $NO_3^- + ClONO_2 + H_2 \rightarrow NO_3^-(ClONO_2) + H_2$	3.0 (−10)[a]	232
(2) $CO_3^- + ClONO_2 \rightarrow NO_3^- + ClO + CO_2$	2.1 (−9)	232
(3) $NO_3^-(HNO_3) + ClONO_2 \rightarrow$ products[b]	<2 (−11)[b]	232
(4) $NO_3^-(H_2O) + ClONO_2 \rightarrow NO_3^-(ClONO_2) + H_2O$	1.8 (−9)	232
(5) $NO_3^-(ClONO_2) + H_2O \rightarrow$ products	n.r.[c]	283
(6) $NO_3^-(ClONO_2) + HNO_3 \rightarrow NO_3^-(HNO_3) + ClONO_2$	1.1 (−9)	283
(7) $NO_3^-(ClONO_2) + HCl \rightarrow NO_3^-(HNO_3) + Cl_2$ (94%) $\rightarrow NO_3^-(HCl) + ClONO_2$ (6%)	1.5 (−9)	283
(8) $NO_3^-(HCl) + ClONO_2 \rightarrow NO_3^-(HNO_3) + Cl_2$ (98%)[d] $\rightarrow NO_3^-(ClONO_2) + HCl$ (2%)	1.8 (−9)	233
(9) $H_3O^+ + ClONO_2 \rightarrow H^+ \cdot ClONO_2 + H_2O$ (31%)[e] $\rightarrow NO_2^+ + H_2OHOCl$ (6%)[e,f] $\rightarrow NO_2^+(H_2O) + HOCl$ (63%)[e]	2.9 (−9)	233
(10) $H_3O^+(H_2O) + ClONO_2 \rightarrow$ products[g]	<1.3 (−10)[g]	233
(11) $H_3O^+(H_2O)_2 + ClONO_2 \rightarrow$ products	n.r.[c]	233
(12) $H_3O^+(H_2O)_3 + ClONO_2 \rightarrow$ products	n.r.[c]	233

[a] 3.0 (−10) means 3×10^{-10}.
[b] No product observed.
[c] No reaction, no decline in reactant ion signal.
[d] Estimated effect of HNO_3 impurity is less than 1 percentage point.
[e] Branching ratio not corrected for HNO_3 impurity, correction will increase $H^+ \cdot ClONO_2$ with respect to the other products.
[f] Neutral product is written as a dimer since monomer formation is endothermic by 0.4 eV. Dimer bond strength is unknown but formation should make the reaction close to thermoneutral.
[g] HNO_3 impurity could account for the reactivity.

preciably with $ClONO_2$, and it is therefore expected that the higher clusters are unreactive as well. The more stable ions $HSO_4^-(H_2SO_4)_m(HNO_3)_n$ also are not expected to react.

CO_3^- and $CO_3^-(H_2O)$ have been used successfully to monitor the concentrations of NO, NO_2, HNO_2, and HNO_3 [*Arnold et al.*, 1992]. Here we find that CO_3^- reacts rapidly with $ClONO_2$ to form NO_3^-. However, this is not a useful reaction for detecting the presence of $ClONO_2$ since NO, NO_2, N_2O_5, and HNO_3 also form NO_3^- from reaction with CO_3^- [*Ikezoe et al.*, 1987]. In fact, the reaction of $ClONO_2$ with CO_3^- may obscure or complicate the detection of some of these other species when $ClONO_2$ concentrations are comparable to that of the nitrogen oxide species of interest.

Another series of ions that is easy to create in active ion source measurements is NO_3^- and its hydrates, $NO_3^-(H_2O)_n$, particularly the first hydrate (where $n = 1$). The present results show that both NO_3^- and $NO_3^-(H_2O)$ react with $ClONO_2$ to form $NO_3^-(ClONO_2)$. These reactions each form an ion, which can be uniquely connected with the presence of $ClONO_2$, an important condition for the accurate determination of atmospheric concentrations. The clustering rate between NO_3^- and $ClONO_2$ is relatively slow and would appear to reduce the sensitivity of using this reaction as a $ClONO_2$ detector. One must note, however, that our results refer to a pressure of only 0.2 torr, while the region of interest for atmospheric detection of $ClONO_2$, 10-25 km, has a pressure of ~20 − 200 torr. One expects that this reaction will saturate under atmospheric conditions and cluster at approximately the collision rate, that is, the rate constant will be the same as that for $NO_3^-(H_2O)$. Direct measurements of this rate constant in a high-pressure apparatus are needed to verify this assumption. In summary, $NO_3^-(ClONO_2)$ should be formed very rapidly by both NO_3^- and $NO_3^-(H_2O)$ under atmospheric conditions.

While this scheme includes a rapid means of forming an ion species that can be attributed unambiguously to $ClONO_2$, there are potentially interfering reactions. Fortunately, H_2O does not react with $NO_3^-(ClONO_2)$. If this reaction were to proceed, the large abundance of H_2O in the atmosphere would ensure that $NO_3^-(ClONO_2)$ would be lost before it could be detected. There are nevertheless several reactions that could interfere with this detection scheme. HNO_3 switches $ClONO_2$ out of $NO_3^-(ClONO_2)$ rapidly to form $NO_3^-(HNO_3)$. HCl reacts with $NO_3^-(ClONO_2)$ to form $NO_3^-(HNO_3)$. This last reaction and the reaction of $NO_3^-(HCl)$ with $ClONO_2$ are analogous to the neutral heterogeneous reaction of $ClONO_2$ with HCl which is important in the mechanism of stratospheric ozone loss in the polar winter. These reactions are discussed in detail in a separate publication [*Van Doren et al.*, 1994].

The ion chemical detection scheme derived from our measurements for determining the concentration of ambient $ClONO_2$ is as follows. A chemical ionization source is set up to produce NO_3^- and $NO_3^-(H_2O)$ as the primary ions. These ions are injected into a flow reactor connected to a mass spectrometer. In the flow tube, reactions (1) and (4) both produce $NO_3^-(ClONO_2)$. The rate constants for both of these reactions are expected to be large at stratospheric temperatures and pressures and for the present purposes can be assumed to be equal to the rate constant for reaction (4). Total depletion of the NO_3^- and $NO_3^-(H_2O)$ primary ions must be kept small, that is, less than 10%. This ensures that

no appreciable secondary reaction of $NO_3^-(ClONO_2)$ will occur; that is, the derived concentration will not be affected by secondary reactions by more than 10%. For low total depletion of primary ions, the concentration of $ClONO_2$ is given as

$$[ClONO_2] = \frac{[NO_3^-(ClONO_2)]}{([NO_3^-]+[NO_3^-(H_2O)])*1.8(-9)*t}, \quad (13)$$

where t is the reaction time in the flow tube and the $ClONO_2$ concentration is in the units of molecule cm^{-3}. It should be noted that only relative ion signals need to be measured.

The concentration detection limit of this scheme can be estimated as follows: The minimum ion ratio that can be detected in mass spectrometers of the type used for in situ atmospheric ion detection by the Arnold and Eisele groups is on the order of 10^{-4}. Typical reaction times in these instruments are 10 ms [*Viggiano*, 1993]. These parameters yield a detection limit of 10^7 molecules cm^{-3}. This estimate has been confirmed by F. Arnold (private communication, 1993) currently the only active researcher flying the type of instrument needed for these measurements. Estimated $ClONO_2$ concentrations in the atmosphere are in the part per billion range, or 4×10^9 molecules cm^{-3} at 15 km. The minimum detection limit of the detection scheme presented greatly exceeds that needed to make measurements of typical concentrations of atmospheric $ClONO_2$ and indicates that accurate measurements can be made under conditions where the $ClONO_2$ concentration is extremely small. When ClO concentrations are comparable to or greater than $ClONO_2$ concentrations, it may also be possible to detect ClO by this technique by titrating the ClO with NO_2.

In addition to the direct determination of atmospheric $ClONO_2$ concentrations, this method is likely to provide simultaneous determinations of the concentrations of other important species such as HCl, HOCl, HNO_3, HNO_2, and H_2SO_4. Such determinations are possible because most acids cluster to NO_3^- and switch H_2O out of $NO_3^-(H_2O)$ [*Ikezoe et al.*, 1987]. The acids HNO_3, HCl, and HNO_2 have been measured by this or similar techniques previously [*Viggiano*, 1993]. For several of these species the rate constants needed are not known, and future work will focus on measuring the pertinent rate coefficients. The most accurate measurements would involve in-flight calibration using controlled releases of the compounds of interest into the flow tube. Such calibrations are currently possible.

Acknowledgments. We would like to thank Steve Lloyd and Jim Anderson for supplying the $ClONO_2$. We also thank Frank Arnold, Ross Salawitch, Eric Hintse, Mark Zahniser, Randy May, David Hanson, and Carl Howard for helpful discussions and encouragement.

References

Arnold, F., et al., Measurements of jet aircraft emissions at cruise altitude, I, The odd nitrogen gases NO, NO_2, HNO_2, and HNO_3. *Geophys. Res. Lett.*, *19*, 2421, 1992.

Ferguson, E. E., and F. Arnold, Ion chemistry of the stratosphere, *Accounts Chem. Res.*, *14*, 327, 1981.

Ikezoe, Y., et al. Gas Phase Ion-Molecule Reaction Rate Constants Through 1986, Maruzen Company, Ltd., Tokyo, 1987.

Keesee, R. G., and A. W. Castleman, Jr., Thermochemical data on gas-phase ion-molecule association and clustering reactions, *J. Phys. Chem. Ref. Data*, *15*, 1011, 1986.

Lloyd, S. A., Issues in stratospheric ozone depletion, Ph.D. thesis, Harvard Univ., Cambridge, Mass., 1993.

Miller, R. H., et al., Infrared spectra of isotopic halogen nitrates, *Spectrochim. Acta*, *23A*, 223–236, 1967.

Raper, O. F., et al., Infrared spectroscopic measurements of halogenated sink and reservoir gases in the stratosphere with the ATMOS instrument, *J. Geophys. Res.*, *92*, 9851, 1987.

Rinsland, C. P., et al., Tentative identification of the 780-cm^{-1} ν_4 band Q branch of chlorine nitrate in high resolution solar absorption spectra of the stratosphere, *J. Geophys. Res.*, *90*, 7931, 1985.

Rodriguez, J. M., Probing stratospheric ozone. *Science*, *261*, 1128, 1993.

Salawitch, R. J., et al., Chemical loss of ozone in the arctic polar vortex in the winter of 1991–1992. *Science*, *261*, 1146, 1993.

Shack, C. J., A new synthesis for chlorine nitrate, *Inorg. Chem.*, *6*, 1938, 1967.

Smith, D., and N. G. Adams, The selected ion flow tube (SIFT): Studies of ion-neutral reactions, *Adv. At. Molec. Phys.*, *24*, 1, 1988.

Toon, O., et al., Heterogeneous reaction probabilities, solubilities, and the physical state of cold volcanic aerosols, *Science*, *261*, 1136, 1933.

Van Doren, J. M., et al., Rate enhancement of the reactions of HCl with ClONO2 and H2O with ClONO2 by ions: Implications for the heterogeneous reactions important in the stratosphere," *J. Am. Chem. Soc.*, in press, 1994.

Viggiano, A. A., Three-body ion-molecule association rate coefficients as a function of temperature and cluster size: $NO_3^-(HNO_3)_n$ + HCl + M → $NO_3^-(HNO_3)_n(HCl)$ + M, *J. Chem. Phys.*, *81*, 2639, 1984.

Viggiano, A. A., In situ mass spectrometry and ion chemistry in the stratosphere and troposphere, *Mass Spectrom. Rev.*, *12*, 115, 1993.

Viggiano, A. A. and F. Arnold, Stratospheric negative ions—Detailed height profiles, *Planet. Space. Sci.*, *31*, 813, 1983.

Viggiano, A. A., et al., Kinetic energy, temperature, and derived rotational temperature dependences for the reaction of $Kr^+(^2P_{3/2})$ and Ar^+ with HCl, *J. Chem. Phys.*, *93*, 1149, 1990.

Webster, C. R., et al., Chlorine chemistry on polar stratospheric cloud particles in the arctic winter, *Science*, *261*, 1130, 1993.

R. A. Morris and A. A. Viggiano, Phillips Laboratory, Geophysics Directorate, Ionospheric Effects Division, 29 Randolph Road, Hanscom Air Force Base, MA 01731-3010.

J. M. Van Doren, Department of Chemistry, College of the Holy Cross, 1 Cross Street, Worcester, MA 01610-2395.

(Received September 24, 1993; revised February 8, 1994; accepted February 8, 1994.)